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(54) BLOCK COPOLYMER COMPOSITION, AND ITS HEAT-SHRINKABLE FILM AND HEAT-SHRINKABLE MULTILAYER FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a heat-shrinkable film excellent in stiffness, heat shrinking properties, slipping properties, anti-blocking properties and printing properties, and to provide a heat-shrinkable multilayer film excellent in interlayer adhesive properties.

SOLUTION: A resin composition is obtained by adding a specific amount of a slip additive, in which methyl polysiloxane as an essential ingredient and as required at least one or more selected from fatty acid amides and hydrocarbon waxes are formulated, to a polymer (composition) composed almost exclusively of a copolymer of a specific vinyl aromatic hydrocarbon and a conjugated diene. A film obtained from the resin composition is oriented to form the heat-shrinkable film, and the film is further used as an outer layer to form the heat-shrinkable multilayer film.

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CLAIMS

[Claim(s)]

[Claim 1]A block copolymer composition thing which contains the following (a), (b), and (c), and is characterized by being formed of 50 - 100 mass part, 0 - 50 mass part, and an ingredient which (c) becomes from (a) and 0.1 per peace 100 mass part of (b) - 1.2 mass part.

(a) At least one sort of vinyl-aromatic-hydrocarbons system polymer (i) vinyl-aromatic-hydrocarbons polymers in which a mass ratio of vinyl aromatic hydrocarbons and conjugated diene was chosen from (i) thru/or (iv) of the block copolymer (b) following which is 60-90:40-10. (ii) Make indispensable a (v) ingredient of the copolymer (iv) rubber denaturation styrene system polymer (c) following which consists of vinyl aromatic hydrocarbons, copolymer (iii) vinyl aromatic hydrocarbons which consist of acrylic acid (meta), and acrylic ester (meta), Lubricant (v) methylphenyl polysiloxane (vi) fatty acid AMAIDO (vii) hydrocarbon wax which blended (vi) and/or (vii) if needed [Claim 2](a) The block copolymer composition thing according to claim 1, wherein number average molecular weights of a vinyl-aromatic-hydrocarbons block of a block rate of a block copolymer after 70 to 90 mass % and ozone degradation are 10,000-50,000.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]The heat contraction nature film this invention excelled [film] in rigidity, heat contraction nature, slippage, blocking resistance, and printing nature, It is related with the resin composition containing the block copolymer which consists of the heat contraction nature multilayer film excellent in the adhesion between layers and vinyl aromatic hydrocarbons which can provide these characteristics, and conjugated diene.

[0002]

[Description of the Prior Art]Conventionally, the result after heat contraction nature or contraction is good for the heat contraction nature film used as the shrink package and shrink label of a container, and the film which fabricated the styrene butadiene series block copolymer is used for it from the point which does not have an environmental pollution problem like polyvinyl chloride in the case of abandonment, either. However, there is a problem of its adhesiveness being high since this film contains butadiene, and being easy to block films. In order to solve this problem, the method of adding silica gel to JP,52-130852,A and adding hydrocarbon wax to JP,1-304146,A is indicated, but by these methods, although blocking resistance improves, there is a fault of being inferior to printing nature. There is a problem that this film is softly limp and that natural contraction is large, and various multilayer films are proposed that these faults should be improved (JP,9-114380,A, JP,11-77916,A). However, the shift of lubricant to inner layer resin from external layer resin takes place, and these films have the problem that a surface characteristic is inferior, compared with the film which produced the film with an external-layer-resin independent. Although adding lubricant so much to external layer resin as the measure is also considered, if too abundant, the problem that printing nature is inferior will arise. When a multilayer is used, the problem that the adhesion between layers is inferior is also produced.

[0003]

[Problem(s) to be Solved by the Invention]An object of this invention is for the block copolymer composition thing which can provide the film excellent in rigidity, heat contraction nature, slippage, blocking resistance, printing nature, and the adhesion between **** and its heat contraction nature film, and a heat contraction nature multilayer film to provide based on the above situations.

[0004]

[Means for Solving the Problem]By making specific vinyl aromatic hydrocarbons and a copolymer of

conjugated diene into a subject, and using a constituent which obtained specific lubricant by carrying out specific amount combination, as a result of repeating research wholeheartedly so that this invention persons may achieve this purpose, It finds out that a heat contraction nature film and a heat contraction nature multilayer film excellent in rigidity, heat contraction nature, and a surface characteristic are obtained, and came to complete this invention.

[0005] This invention contains the following (a), (b), and (c), and Namely, 50 - 100 mass part, (b) Zero to 50 mass part, and a block copolymer composition thing currently formed of an ingredient which (c) becomes from (a) and 0.1 per piece 100 mass part of (b) - 1.2 mass part, A heat contraction nature film and at least one outer layer which extend the constituent concerned are related with a heat contraction nature multilayer film currently formed with the constituent concerned.

(a) At least one sort of vinyl-aromatic-hydrocarbons system polymer (i) vinyl-aromatic-hydrocarbons polymers in which a mass ratio of vinyl aromatic hydrocarbons and conjugated diene was chosen from (i) thru/or (iv) of the block copolymer (b) following which is 60-90:40-10. (ii) Make indispensable (v) of the copolymer (iv) rubber denaturation styrene system polymer (c) following which consists of vinyl aromatic hydrocarbons, copolymer (iii) vinyl aromatic hydrocarbons which consist of acrylic acid (meta), and acrylic ester (meta), Lubricant (v) methylphenyl polysiloxane (vi) fatty acid AMAIDO (vii) hydrocarbon wax which blended (vi) and/or (vii) if needed [0006] Mass ratios of vinyl aromatic hydrocarbons and conjugated diene of the (a) block copolymer are 60-90:40-10. It is preferred that molecular weights of a vinyl-aromatic-hydrocarbons block of a block rate after 70 to 90 mass % and ozone degradation are 10,000-50,000. In a heat contraction nature multilayer film, A inner layer or other layers in the case of a bilayer a layer formed from at least one sort of styrene system polymers chosen from a block copolymer and/or (b) vinyl-aromatic-hydrocarbons system polymer which consist of following (d) (viii) vinyl aromatic hydrocarbons and conjugated diene. It is preferred that it is a heat contraction nature multilayer film which it has.

(d) A styrene system polymer. (viii) A copolymer which consists of vinyl aromatic hydrocarbons, the block copolymer (i) vinyl-aromatic-hydrocarbons polymer (ii) vinyl aromatic hydrocarbons which consist of conjugated dienes, copolymer (iii) vinyl aromatic hydrocarbons which consist of acrylic acid (meta), and acrylic ester (meta). (iv) As a rubber denaturation styrene system polymer, a heat contraction nature film, and a heat contraction nature multilayer film, it is preferred that coefficients of static friction of much more film surface are especially 0.2-0.5 at least.

[0007] This invention is explained in detail below. As (a) vinyl aromatic hydrocarbons used by this invention, and vinyl aromatic hydrocarbons used for a block copolymer of conjugated diene, Although styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, alpha-methylstyrene, vinylnaphthalene, vinylanthracene, etc. can be mentioned, Generally styrene is mentioned especially.

[0008] As conjugated diene used for manufacture of a block copolymer of (a) used by this invention, Although 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, etc. are mentioned, as a general thing, 1,3-butadiene and isoprene are mentioned especially.

[0009] The aforementioned vinyl aromatic hydrocarbons and a mass ratio of conjugated diene are 60-90:40-10, and are 70-85:30-15 preferably. Since extension temperature at the time of film manufacture becomes high and the heat contraction nature of a film is inferior when the rigidity of a film exceeds 90

mass % by less than 60 mass % in a mass ratio of vinyl aromatic hydrocarbons, there is no **** in practical use.

[0010]As for a block rate of vinyl aromatic hydrocarbons of a block copolymer of (a), it is preferred that it is 70 - 90 mass %. The rigidity of a film falls that a block rate is less than 70 mass %, and since shift to the surface of lubricant does not progress but it is inferior to a surface characteristic when 90 mass % is exceeded, there is a tendency which is not in practical use in ****. A block rate of vinyl aromatic hydrocarbons is searched for with a following formula. That is, it is block rate (%) = $(W1/W0) \times 100$. Mass of a block polymerization chain of vinyl aromatic hydrocarbons in a copolymer and W0 show full weight of vinyl aromatic hydrocarbons in a block copolymer W1 here. W1 in said formula carries out [with a publicly known literature "rubber chemistry and technology (Y. TANAKA, et al., RUBBERCHEMISTRY AND TECHNOLOGY)" of 58 or 16 pages (1985)] ozone degradation of the block copolymer by a method of a statement, Gel permeation chromatograph (it abbreviates to GPC below) measurement of the obtained vinyl-aromatic-hydrocarbons polymer component is carried out, It asked from an analytical curve which created a molecular weight corresponding to chromatogram using standard polystyrene and a styrene oligomer, and quantified and asked for a thing exceeding the number average molecular weight 3,000 from a peak area. An ultraviolet spectroscopy detector which set wavelength as 254 nm was used as a detector.

[0011]As for a number average molecular weight of a vinyl-aromatic-hydrocarbons block after the aforementioned ozone degradation, it is preferred that it is 10,000-50,000. When there are two or more peaks of a molecular weight, it is an average molecular weight of these whole. Since shift to a film surface of lubricant does not progress but blocking resistance is inferior when printing nature falls and 50,000 is exceeded, in order that shift to a film surface of lubricant may progress too much by less than 10,000 in a molecular weight, there is a tendency which is not in practical use, respectively in ****. It is 10,000-40,000 preferably.

[0012]Next, manufacture of a block copolymer of (a) of this invention is explained. A block copolymer of (a) is obtained by polymerizing vinyl aromatic hydrocarbons and conjugated diene by using an organolithium compound as an initiator in an organic solvent. As an organic solvent, butane, pentane, hexane, isopentane, heptane, Aliphatic hydrocarbon, such as octane and isooctane, cyclopentane, methylcyclopentane, Publicly known organic solvents, such as aromatic hydrocarbon, such as alicyclic hydrocarbon, such as cyclohexane, a methylcyclohexane, and ethylcyclohexane, or benzene, toluene, ethylbenzene, and xylene, can be used.

[0013]An organolithium compound is a compound which one or more lithium atoms combined in a molecule, For example, ethyllithium, n-propyllithium, isopropyllithium, A polyfunctional organolithium compound like a monofunctional organolithium compound like n-butyl lithium, sec-butyl lithium, and t-butyl lithium, hexamethylene dilithium, butadienyl dilithium, and isoprenyldilithium can be used.

[0014]Although vinyl aromatic hydrocarbons and conjugated diene which are used for this invention can use the thing, they can choose one sort or two sorts or more, respectively, and can use them for a polymerization. And in living anionic polymerization which uses the aforementioned organolithium compound as an initiator, the whole quantity converts mostly into a polymer vinyl aromatic hydrocarbons and conjugated diene with which a polymerization reaction was presented.

[0015]A block rate of vinyl aromatic hydrocarbons of a block copolymer of (a) is controllable by an addition

of a randomization agent at the time of carrying out copolymerization of vinyl aromatic hydrocarbons and the conjugated diene. Although a tetrahydrofuran (THF) is mainly used as a randomization agent, an alkoxide of other ether, amines and thioether, phosphor amide, alkylbenzene sulfonates, potassium, or sodium, etc. can be used.

[0016]As suitable ether of a randomization agent, wood ether, diethylether, diphenyl ether, diethylene glycol dimethyl ether, diethylene-glycol dibutyl ether, etc. other than THF are mentioned. As amines, cyclic amine besides a tertiary amine, for example, trimethylamine, triethylamine, and tetramethylethylenediamine etc. can be used. In addition, triphenyl phosphine, hexamethylphosphoramide, potassium alkylbenzene sulfonate or sodium, potassium, or sodium butoxide can be used as a randomization agent.

[0017]As an addition of a randomization agent, 0.001 to 10 mass part is preferred to all the brewing monomer 100 mass part. An addition stage may be before a start of a polymerization reaction, and may be before a polymerization of a copolymerization chain of vinyl aromatic hydrocarbons and conjugated diene. Additional addition can also be carried out if needed.

[0018]In addition, a block rate is controllable also by carrying out continuation feeding of vinyl aromatic hydrocarbons and the conjugated diene mechanically at a polymerization can, or *(ing) vinyl aromatic hydrocarbons and conjugated diene by every in small quantities by turns to a polymerization can.

[0019]A molecular weight of a vinyl-aromatic-hydrocarbons block after ozone degradation of a block copolymer of (a) is controllable by ratio of an initiator to a monomer, and a ratio of vinyl aromatic hydrocarbons to conjugated diene.

[0020]Thus, an obtained block copolymer is inactivated by adding sufficient quantity for making an active terminal inactivate terminators, such as water, alcohol, and carbon dioxide. As a method of collecting copolymers from an obtained block copolymer solution, ** How to evaporate a solvent with a method, ** heating roller, etc. which are deposited with poor solvents, such as methanol, and deposit (the drum dryer method), ** After condensing a solution with a concentrator, water is made to distribute a method and ** solution from which a solvent is removed with a vent type extruder, and arbitrary methods, such as a method (the steam stripping method) of blowing a steam, carrying out heating removal of the solvent, and collecting copolymers, can be adopted.

[0021]A vinyl-aromatic-hydrocarbons system polymer of (b) used by this invention, (i) A vinyl-aromatic-hydrocarbons polymer, a copolymer which consists of (ii) vinyl aromatic hydrocarbons and acrylic acid (meta), (iii) They are at least one sort of polymers chosen from a copolymer and a (iv) rubber denaturation styrene system polymer which consist of vinyl aromatic hydrocarbons and acrylic ester (meta).

[0022](i) As a vinyl-aromatic-hydrocarbons polymer, a homopolymer of the aforementioned vinyl aromatic hydrocarbons or two or more sorts of copolymers are used. Polystyrene is especially mentioned as a general thing.

[0023](ii) although a copolymer which consists of vinyl aromatic hydrocarbons and acrylic acid (meta-) is obtained by polymerizing aforementioned vinyl aromatic hydrocarbons and acrylic acid (meta-) -- a polymerization -- each monomer -- respectively -- one sort -- or two or more sorts can be chosen and it can use.

[0024](Meta) Acrylic acid and methacrylic acid are mentioned as acrylic acid.

[0025](iii) although a copolymer which consists of vinyl aromatic hydrocarbons and acrylic ester (meta-) is

obtained by polymerizing aforementioned vinyl aromatic hydrocarbons and acrylic ester (meta-) -- a polymerization -- each monomer -- respectively -- one sort -- or two or more sorts can be chosen and it can use.

[0026](Meta) As acrylic ester, methyl acrylate, ethyl acrylate, Acrylic acid-n-butyl, isobutyl acrylate, acrylic acid hexyl, acrylic acid (2-ethyl) hexyl, methyl methacrylate, ethyl methacrylate, butyl methacrylate, methacrylic acid (2-hydroxy) ethyl, etc. are mentioned.

[0027]A copolymer of said (ii) or (iii), a mass ratio of vinyl aromatic hydrocarbons, acrylic acid (meta-) or vinyl aromatic hydrocarbons, and acrylic ester (meta-) -- 5-99:95-1 -- 40-99:60-1, and a monomer mixture that are 70-99:30-1 still more preferably are polymerized and obtained preferably.

[0028](iv) A rubber denaturation styrene system polymer is obtained by polymerizing a mixture of vinyl aromatic hydrocarbons or this and a copolymerizable monomer, and various elastomers. As vinyl aromatic hydrocarbons, what was explained with the aforementioned block copolymer of (a) is used. As this and a copolymerizable monomer, the acrylic acid (meta), acrylic ester (meta), acrylonitrile, etc. are mentioned. As an elastomer, butadiene rubber, a styrene butadiene rubber, a styrene butadiene block copolymer elastomer, chloroprene rubber, crude rubber, etc. are used. As a desirable rubber denaturation styrene system polymer, shock-proof rubber denaturation styrene resin (HIPS), MBS resin, and MBAS resin are mentioned especially.

[0029]MBS resin and MBAS resin manufacture copolymer rubber latex with styrene which uses polybutadiene or butadiene as the main ingredients first with a publicly known emulsion polymerization method. In this case, a cross linking agent and a chain transfer agent may be used. Next, MBS resin adds styrene, methyl methacrylate, and/or alkyl acrylate to this rubber latex, MBAS resin adds styrene, methyl methacrylate, acrylonitrile, and/or alkyl acrylate, and it is obtained by performing graft polymerization. Alkyl acrylate which stated alkyl acrylate used for MBS resin and MBAS resin with a copolymer which consists of aforementioned (iii) vinyl aromatic hydrocarbons and acrylic ester (meta) is mentioned.

[0030]In this invention, mass ratios of a block copolymer of (a) and a vinyl-aromatic-hydrocarbons system copolymer of (b) are 50-100:0-50, are 55-100:0-45 preferably, and are 60-100:0-40 still more preferably. Since extension temperature at the time of film manufacture becomes high by less than 50 mass % in a block copolymer of (a) and the heat contraction nature of a film is inferior, there is no **** in practical use.

[0031]Lubricant of (c) used by this invention is the lubricant which blended at least one sort which used a (v) methylphenyl polysiloxane as an essential ingredient, and was chosen from (vi) fatty acid AMAIDO and a (vii) hydrocarbon system wax if needed. It is the lubricant which blended at least one sort which used a (v) methylphenyl polysiloxane as an essential ingredient preferably, and was chosen from (vi) fatty acid AMAIDO and a (vii) hydrocarbon system wax.

[0032](v) As a methylphenyl polysiloxane, although there is no limitation in particular, viscosity [in / still more preferably / 50 to 5,000 centistokes / in viscosity at temperature of 25 ** / temperature of 25 **] is a thing of 100 to 3,000 centistokes preferably.

[0033]As fatty acid AMAIDO, (vi) Lauric acid AMAIDO, palmitic acid AMAIDO, Saturated fatty acid mono-AMAIDO, such as stearic acid AMAIDO, behenic acid AMAIDO, and hydroxystearic acid AMAIDO, Unsaturated fatty acid mono- AMAIDO, such as oleic acid AMAIDO, erucic acid AMAIDO, and ricinoleic acid AMAIDO, N-stearylstearic acid AMAIDO, N-oleyloleic acid AMAIDO, N-stearyleoleic acid AMAIDO, N-oleylstearic acid AMAIDO, N-stearylerucic acid AMAIDO, N-oleylpalmitic acid AMAIDO, Substitution

AMAIDO, such as methylolstearic acid AMAIDO and methylolbehenic acid AMAIDO. Methylenebis stearic acid AMAIDO, ethylene VISCA purine acid AMAIDO, Ethylene screw lauric acid AMAIDO, ethylene screw stearic acid AMAIDO, Ethylene screw isostearic acid AMAIDO, ethylene screw hydroxystearic acid AMAIDO, Saturated fatty acid screw AMAIDO, such as ethylene screw behenic acid AMAIDO, hexa methylenebis hydroxystearic acid AMAIDO, N,N'-distearyl adipic acid AMAIDO, and N,N'-distearyl sebacic acid AMAIDO, ethylene screw oleic acid AMAIDO, Hexa methylenebis oleic acid AMAIDO, N,N'-dioleoyl adipic acid AMAIDO, Aromatic screw AMAIDO, such as unsaturated fatty acid screw AMAIDO, such as N,N'-dioleoyl sebacic acid AMAIDO, m-xylylene screw stearic acid AMAIDO, and N,N'-distearyl isophthalic acid AMAIDO, may be mentioned, these may be used alone, and two or more sorts may be used together. Ethylene screw stearic acid AMAIDO, erucic acid AMAIDO, and stearic acid AMAIDO are especially preferred.

[0034]As hydrocarbon wax, (vii) A rice wax, beeswax, A montan wax, paraffin wax, microcrystallin wax, Denaturation polyethylene wax, such as the Fischer Tropsch wax, polyethylene wax, and oxidized polyethylene wax, hardening castor oil, etc. may be mentioned, these may be used alone, and two or more sorts may be used together. Polyethylene wax, oxidized polyethylene wax, and the Fischer Tropsch wax are especially preferred.

[0035]In this invention, loadings of lubricant of (c) are 0.1 per peace 100 mass part of a block copolymer of (a), and a vinyl-aromatic-hydrocarbons system polymer of (b) - 1.2 mass part, and it is preferred that it is 0.15 - 1.1 mass part preferably. At less than 0.1 mass parts, since slippage runs short and blocking resistance is inferior, a film sticks and there is no **** in practical use. Since printing nature will worsen if 1.2 mass parts are exceeded, there is no **** in practical use. When (c) lubricant consists of a (v) methylphenyl polysiloxane and (vi) fatty acid AMAIDO, it is preferred that (vi) fatty acid AMAIDO is 0.5 or less (however, zero mass part does not contain) mass parts. When becoming a (v) methylphenyl polysiloxane from (vii) hydrocarbon wax, it is preferred that (vii) hydrocarbon wax is 0.5 or less (however, zero mass part does not contain) mass parts. When (c) lubricant consists of a (v) methylphenyl polysiloxane, (vi) fatty acid AMAIDO, and (vii) hydrocarbon wax, (vi) It is preferred that fatty acid AMAIDO is [(vii) hydrocarbon wax] 0.5 or less (however, zero mass part does not contain) mass parts in 0.5 or less (however, zero mass part does not contain) mass parts.

[0036]Various additive agents can be blended with a block copolymer composition thing of this invention if needed. As an additive agent, various stabilizer, processing aid, a light resistance improver, a softener, a plasticizer, a spray for preventing static electricity, an antifogger, mineral oil, a filler, paints, fire retardant, etc. are mentioned.

[0037]As the above-mentioned stabilizer, 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl) ethyl]-4,6-di-tert-pentylphenyl acrylate, Phosphorus system antioxidants, such as phenolic antioxidants, such as 2,6-di-tert-butyl-4-methyl phenol, and tris nonylphenyl phosphite, etc. are mentioned. A publicly known thing which has general processing aid, light resistance improver, softener, plasticizer, spray for preventing static electricity, antifogger, mineral oil, filler, paints, fire retardant, etc. is mentioned.

[0038]Although a constituent of this invention is obtained by mixing (c) with (a), (c) and (a), and (b), Although there is no regulation in particular, the dry blend of the mixing method may be carried out, for example with a Henschel mixer, a ribbon blender, V blender, etc., and also with an extrusion machine, it

may be melting-ized and may be pelletized. Or it may add in stages, such as post-processing of a polymer, before a polymerization start in the middle of a polymerization reaction at the time of manufacture of each polymer. When blending an additive agent if needed, these additive agents can be blended with the above (a), (b), and (c) at a further predetermined rate, for example, and it can be based on the same mixing method as the above.

[0039]A heat contraction nature film of this invention is obtained by extending a sheet and a film which were extruded by publicly known method, for example, a T-die method, and the tubular method to one axis, two axes, or a multiple spindle using the above-mentioned constituent concerned.

[0040]In using a constituent of this invention as an outer layer of a heat contraction nature multilayer film, It is a film layer which consists of a styrene system polymer preferably although not limited to one outer layer in particular in the case of a inner layer or a bilayer, A film layer formed with a block copolymer which consists of vinyl aromatic hydrocarbons and conjugated diene, a vinyl-aromatic-hydrocarbons system polymer explained by (b), ABS plastics, a styrene acrylonitrile copolymer, etc. is mentioned. A polymer (resin is also included) used for these films may be used alone, and may be used together. A polymer used preferably is a vinyl-aromatic-hydrocarbons system polymer explained by a block copolymer which consists of (viii) vinyl aromatic hydrocarbons and conjugated diene, and/or (b), (i) A vinyl-aromatic-hydrocarbons polymer, a copolymer which consists of (ii) vinyl aromatic hydrocarbons and acrylic acid (meta), (iii) They are at least one sort of polymers chosen from a copolymer and a (iv) rubber denaturation styrene system polymer which consist of vinyl aromatic hydrocarbons and acrylic ester (meta). A block copolymer which consists of (viii) vinyl aromatic hydrocarbons and conjugated diene may be the same as a block copolymer which consists of vinyl aromatic hydrocarbons used by (a), and conjugated diene, or may differ. A styrene butadiene block copolymer which is especially different from a polymer used as (a) preferably is mentioned. The above-mentioned vinyl-aromatic-hydrocarbons system polymer used as (d) may also be the same as a vinyl-aromatic-hydrocarbons system polymer of (b), or it may differ. Various additive agents as well as the above can be blended. These mixing methods can also be depended on the same mixing method as the above.

[0041]A heat contraction nature multilayer film of this invention fuses the above-mentioned resin with an extrusion machine respectively an object for rear surface layers, and for interlayers, and is obtained by extending it to one axis, two axes, or a multiple spindle after multilayering by the inside of a die, or a feed block. Publicly known things, such as a T die and an annular die, can be used for a die used with a heat contraction nature film and a heat contraction nature multilayer film. A method of extending a extruded sheet as an example of uniaxial stretching in the direction which intersects perpendicularly with an extrusion direction by a tenter, a method of extending a extruded tubular film to a circumferencial direction, etc. are mentioned. After extending a extruded sheet to an extrusion direction with a roll as an example of biaxial stretching, a method of extending in the direction which intersects perpendicularly with an extrusion direction by a tenter etc., a method of extending a extruded tubular film simultaneous or independently to an extrusion direction and a circumferencial direction, etc. are mentioned. It is easy to be natural, even if it comes out further as a inner layer in a multilayer film, a certain necessity is not and it is more than a bilayer.

[0042]As for extension temperature, in this invention, 60-120 °C is preferred. Since good shrink characteristics are not acquired when a sheet and a film fracture at 60 °C at the time of extension and it

exceeds 120 **, it is not desirable. Although there is no restriction in particular, 1.5 to 8 times of draw magnification are preferred. In 1.5 times, since extension is difficult when heat contraction nature runs short and it exceeds 8 times, it is not desirable. When using these films as a heat contraction nature label or wrapping, a heat shrinkage rate is required not less than 20% at temperature of 80 **. At 20%, since an elevated temperature is needed at the time of contraction, it has an adverse effect on an article covered, and is not desirable. A desirable heat shrinkage rate is not less than 30% at the temperature. 10-300 micrometers is preferred for thickness of a film.

[0043]As for a coefficient of static friction on at least one surface of an outer layer film of a heat contraction nature film of this invention, and a heat contraction nature multilayer film, it is preferred that it is 0.2-0.5. Since blocking resistance is inferior when 0.5 is exceeded, since printing nature is inferior or a rolled film sideslips, there is no **** in practical use less than 0.2. A coefficient of static friction is controllable by extension temperature, heat setting temperature after extension besides loadings of the above (a), (b), and (c), etc.

[0044]It is preferred that a modulus of elasticity in tension of a heat contraction nature film of this invention and a heat contraction nature multilayer film is more than 1300 (MPa). If smaller than 1300 (MPa), it will be inferior to rigidity and the waist will be easily lost on a film. If it is preferred that it is below 20 (%) as for an ink peeling rate and it is larger than 20 (%), it will become the tendency for a printing surface of a film surface by which printing nature was carried out to exfoliate easily. [of a thing]

[0045]Especially as a use of a heat contraction nature film of this invention, and a heat contraction nature multilayer film, although a heat contraction nature label, a heat contraction nature cap seal, etc. are preferred, it can use for a packaging film etc. suitably.

[0046]

[Example]Next, although this invention is further explained with an example, this invention is not limited to these examples.

[0047]The vinyl-aromatic-hydrocarbons-conjugated diene block copolymer of (a) shown in the one to Examples 1-11 and comparative example 7 table 1, The block copolymer composition thing was manufactured by fusing and pelletizing after mixing the vinyl-aromatic-hydrocarbons system polymer of (b) shown in Table 2, and (c) lubricant shown in Table 3 with an extrusion machine with a Henschel mixer according to the combination formula of Table 5 - 7, respectively. The film carried out extrusion molding of the 0.3-mm-thick sheet at the temperature of 210 ** first, and carried out oriented film creation after that using the biaxial-stretching device by an Oriental energy machine factory company by increasing horizontal uniaxial stretching 5 times at the temperature of 90 **.

[0048]Physical properties were shown in Table 5 - 7 with the loadings (mass part) of each ingredient.

[0049]Examples 12-21 and the comparative example 8 - 12 (**) -- the ingredient for outer layers -- ingredient (a): -- the vinyl-aromatic-hydrocarbons-conjugated diene block copolymer as shown in Table 1 was used.

[0050]

[Table 1]

| 重合体 | 単量体単位の割合 (質量%) | ブロック率 (質量%) | オゾン分解後の 数平均分子量 |
|-----|-------------------|----------------|-------------------|
| a 1 | ブタジエン 16 | 8 4 | 3 0, 0 0 0 |
| | スチレン 84 | | |
| a 2 | ブタジエン 25 | 8 3 | 2 3, 0 0 0 |
| | スチレン 75 | | |
| a 3 | ブタジエン 45 | 7 5 | 2 1, 0 0 0 |
| | スチレン 55 | | |
| a 4 | ブタジエン 5 | 8 8 | 4 8, 0 0 0 |
| | スチレン 95 | | |
| a 5 | ブタジエン 21 | 6 5 | 2 2, 0 0 0 |
| | スチレン 79 | | |
| a 6 | ブタジエン 24 | 9 5 | 4 6, 0 0 0 |
| | スチレン 76 | | |
| a 7 | ブタジエン 26 | 7 2 | 1 5, 0 0 0 |
| | スチレン 74 | | |
| a 8 | ブタジエン 20 | 8 6 | 8 0, 0 0 0 |
| | スチレン 80 | | |

[0051]Ingredient (b): The copolymer which consists of a (i) vinyl-aromatic-hydrocarbons polymer, and (ii) vinyl aromatic hydrocarbons and acrylic acid (meta) as shown in Table 2, the copolymer which consists of (iii) vinyl aromatic hydrocarbons and acrylic ester (meta), and the (iv) rubber denaturation styrene system polymer were used.

[0052]

[Table 2]

| 重合体 | 重合体構造 | 単量体単位の割合 (質量%) | |
|-----|-------------------------------------|----------------|-----|
| b 1 | ポリスチレン | スチレン | 100 |
| b 2 | HIPS | ブタジエン | 7 |
| | | スチレン | 93 |
| b 3 | スチレンー メタクリル酸 | メタクリル酸 | 10 |
| | 共重合体 | スチレン | 90 |
| b 4 | スチレンー n-ブチルアクリレート | n-ブチルアクリレート | 20 |
| | 共重合体 | スチレン | 80 |
| b 5 | スチレンー メチルメタクリレート | メチルメタクリレート | 22 |
| | 共重合体 | スチレン | 78 |
| b 6 | スチレンー n-ブチルアクリレートー メチルメタクリレート | n-ブチルアクリレート | 14 |
| | 共重合体 | メチルメタクリレート | 7 |
| | | スチレン | 79 |

[0053]Ingredient (c): A (v) methylphenyl polysiloxane as shown in Table 3, (vi) fatty acid AMAIDO, and (vii) hydrocarbon wax were used.

[0054]

[Table 3]

| 滑剤 | 構 造 |
|-----|------------------|
| c 1 | メチルフェニルポリシロキサン |
| c 2 | エチレンビスステアリン酸アמיד |
| c 3 | ポリエチレンワックス |

[0055](**) The styrene system polymer as the ingredient for inner layers is shown in Table 4 was used.

[0056]

[Table 4]

| 重合体 | 重合体構造 | 単量体単位の割合（質量％） | |
|-----|------------------|-----------------|-----|
| d 1 | スチレン－ブタジエンブロック | ブタジエン 2 2 | |
| | 共重合体 | スチレン 7 8 | |
| d 2 | ポリスチレン | スチレン 1 0 0 | |
| d 3 | スチレン－n－ブチルアクリレート | n－ブチルアクリレート 1 7 | |
| | 共重合体 | スチレン 8 3 | |
| d 4 | M B S | メチルメタクリレート | 2 1 |
| | | ブタジエン | 4 5 |
| | | n－ブチルアクリレート | 2 |
| | | スチレン | 3 2 |
| d 5 | H I P S | ブタジエン | 7 |
| | | スチレン | 9 3 |

[0057](**) The (a) vinyl-aromatic-hydrocarbons-conjugated diene block copolymer shown in Table 1 as an ingredient for manufacture outer layers of a film, The heat contraction nature multilayer film was created using (b) vinyl-aromatic-hydrocarbons system polymer shown in Table 2, (c) lubricant shown in Table 3, and (d) styrene system polymer shown in Table 4 as an ingredient for inner layers by the loadings (mass part) of the raw material polymer of each class shown in Table 8 - 10, and a layer ratio (%). The polymer or polymer composition corresponding to each class was first fused with the separate extrusion machine, it multilayered within the T die, and the film fabricated the 0.3-mm-thick sheet. Then, oriented film creation was carried out using the biaxial-stretching device by an Oriental energy machine factory company by increasing horizontal uniaxial stretching 5 times at the temperature of 90 **.

[0058]Physical properties were shown in Table 8 - 10 with the loadings (mass part) of the raw material polymer of each class, and a layer ratio (%).

[0059]Each physical properties of the film were based on the following method.

(1) Modulus of elasticity in tension : based on JIS K6871, it measured using the tensilon universal testing machine made from an Ey and day (RTC-1210A).

(2) Heat shrinkage rate : it was immersed for 30 seconds into 80 ** warm water, and computed from the following formula.

Heat-shrinkage-rate (%) = $\{(L1-L2)/L1\} \times 100$, however L1: Length (the extension direction) before immersion, length after the contraction immersed for 30 seconds into L2:80 ** warm water (the extension direction)

Coefficient of static friction : (3) The film started to 10 cm x 6.4 cm at the thread of the friction measuring instrument by an Oriental energy machine factory company (AN type), After setting to a ramp (1 kg of load) the film started to 28 cm x 10 cm, the angle of friction X (degree) was measured and the value of tanX was made into the coefficient of static friction.

(4) Blocking resistance : prepare the film started in size of 35 mm x 50 mm four sheets. This film is piled up, the board of SUS is hit from those both sides, and it binds tight with a bolt. The film piled up after being

immersed in 70 °C warm water for 30 minutes is taken out. The film was horizontally shifted with the finger and the ease of moving was evaluated in the following stage.

O; move easily. **; it is hard to move. x; it does not move.

[0060](5) Ink peeling rate : after applying the ink by a great Nissei-ized company "STR722 (yellow)" to the film and being air-dry for 2 hours, the ink peeling rate was computed with the following formula, and the friction test method of sticking and removing a cellophane tape estimated.

After putting a break into the adhesion profitable **** oriented film between layers of ink peeling rate (%) = (area in which ink separated)/(area of ink coated surface which stuck Scotch tape (registered trademark)) x100 (6) film with scissors, it extended horizontally and detachability was evaluated in the following stage.

O; even if it extends, don't carry out layer exfoliation.

**; if it extends, layer exfoliation will be carried out, but only the layer cannot be removed easily.

x; if it extends, layer exfoliation is carried out and only the layer can be removed easily.

[0061]The heat contraction nature film of this invention is excellent in rigidity, heat contraction nature, slippage, blocking resistance, and printing nature, and also in the case of a heat contraction nature multilayer film, the physical properties shown in Table 5 - 10 show excelling in the adhesion between layers in addition to these characteristics.

[0062]

[Table 5]

| | 実 施 例 | | | | | |
|-------------|-------------|-------------|------------|------------|------------|-------------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| 配合量 (質量部) | a 1 : 1 0 0 | a 1 : 1 0 0 | a 2 : 8 0 | a 2 : 8 5 | a 2 : 6 0 | a 5 : 1 0 0 |
| | | | b 1 : 2 0 | b 3 : 1 5 | b 4 : 4 0 | |
| | | | b 2 : 1 | | | |
| | c 1 : 0.50 | c 1 : 0.70 | c 1 : 0.35 | c 1 : 0.70 | c 1 : 0.80 | c 1 : 0.70 |
| | | c 2 : 0.15 | c 2 : 0.12 | c 2 : 0.10 | c 3 : 0.15 | c 2 : 0.15 |
| | | | | c 3 : 0.10 | | |
| 引張弾性率 (MPa) | 1, 5 1 0 | 1, 5 0 0 | 1, 6 3 0 | 1, 5 8 0 | 1, 8 5 0 | 1, 2 6 0 |
| 熱収縮率 (%) | 4 9 | 4 9 | 4 0 | 4 1 | 4 6 | 4 8 |
| 静止摩擦係数 | 0. 4 0 | 0. 3 0 | 0. 3 8 | 0. 2 3 | 0. 2 1 | 0. 2 7 |
| 耐ブロッキング性 | ○ | ○ | ○ | ○ | ○ | ○ |
| インキ剥離率 (%) | 0 | 0 | 0 | 1 0 | 2 0 | 0 |

[0063]

[Table 6]

| | 実施例 | | | | |
|-------------|------------|------------|------------|------------|------------|
| | 7 | 8 | 9 | 10 | 11 |
| 配合量 (質量部) | a 6 : 100 | a 7 : 100 | a 8 : 100 | a 2 : 88 | a 2 : 82 |
| | | | | b 5 : 12 | b 6 : 18 |
| | | | | | |
| | c 1 : 0.70 | c 1 : 0.70 | c 1 : 0.70 | c 1 : 0.70 | c 1 : 0.70 |
| | c 2 : 0.15 | c 2 : 0.15 | c 2 : 0.15 | c 2 : 0.15 | c 2 : 0.15 |
| 引張弾性率 (MPa) | 1, 880 | 1, 470 | 1, 670 | 1, 540 | 1, 560 |
| 熱収縮率 (%) | 35 | 50 | 41 | 42 | 43 |
| 静止摩擦係数 | 0.46 | 0.21 | 0.48 | 0.34 | 0.32 |
| 耐ブロッキング性 | △ | ○ | △ | ○ | ○ |
| インキ剥離率 (%) | 0 | 20 | 0 | 0 | 0 |

[0064]

[Table 7]

| | 比較例 | | | | | | |
|-------------|------------|---------------------------------------|------------|------------|---------------------------------------|------------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 配合量 (質量部) | a 3 : 100 | a 4 : 100 | a 1 : 100 | a 1 : 100 | a 1 : 40 | a 1 : 100 | a 1 : 100 |
| | | | | | b 1 : 50 | | |
| | | | | | | | |
| | c 1 : 0.70 | c 1 : 0.70 | c 1 : 0.05 | c 1 : 0.70 | c 1 : 0.70 | c 1 : 0.08 | c 1 : 1.4 |
| | c 2 : 0.15 | c 2 : 0.15 | c 2 : 0.03 | c 2 : 0.60 | c 2 : 0.15 | | |
| 引張弾性率 (MPa) | 680 | シート成形 はできたが 延伸フィル ムが得られ ず | 1, 510 | 1, 490 | シート成形 はできたが 延伸フィル ムが得られ ず | 1, 510 | 1, 500 |
| 熱収縮率 (%) | 50 | | 49 | 48 | | 49 | 48 |
| 静止摩擦係数 | 0.25 | | 0.80 | 0.08 | | 0.86 | 0.15 |
| 耐ブロッキング性 | ○ | | × | ○ | | × | ○ |
| インキ剥離率 (%) | 0 | | 0 | 100 | | 0 | 50 |

[0065]

[Table 8]

| | | 実 施 例 | | | | |
|-------------|-----|-------------|-------------|-------------|-------------|------------|
| | | 1 2 | 1 3 | 1 4 | 1 5 | 1 6 |
| 表層および裏層 | 配合量 | a 1 : 1 0 0 | a 1 : 1 0 0 | a 2 : 8 0 | a 1 : 1 0 0 | a 2 : 9 0 |
| | | | | b 1 : 2 0 | b 2 : 1 | b 3 : 1 0 |
| | | c 1 : 0.50 | c 1 : 0.70 | c 1 : 0.35 | c 1 : 0.70 | c 1 : 0.80 |
| | | | c 2 : 0.15 | c 2 : 0.12 | c 2 : 0.10 | c 3 : 0.15 |
| | | | c 3 : 0.10 | | | |
| 中間層 | 配合量 | d 1 : 1 0 0 | d 1 : 1 0 0 | d 1 : 1 0 0 | d 1 : 5 5 | d 1 : 9 0 |
| | | | | d 5 : 1 | d 3 : 4 5 | d 2 : 1 0 |
| 表／中間／裏層比 | | 10/80/10 | 10/80/10 | 10/80/10 | 10/80/10 | 10/80/10 |
| 引張弾性率 (MPa) | | 1, 5 3 0 | 1, 5 2 0 | 1, 6 0 0 | 1, 8 2 0 | 1, 6 5 0 |
| 熱収縮率 (%) | | 4 4 | 4 3 | 4 2 | 4 5 | 4 0 |
| 静止摩擦係数 | | 0. 4 2 | 0. 3 5 | 0. 4 1 | 0. 2 5 | 0. 2 4 |
| 耐ブロッキング性 | | ○ | ○ | ○ | ○ | ○ |
| インキ剥離率 (%) | | 0 | 0 | 0 | 10 | 20 |
| 層間密着性 | | ○ | ○ | ○ | ○ | ○ |

[0066]

[Table 9]

| | | 実 施 例 | | | | |
|-------------|-----|------------|-------------|-------------|-------------|-------------|
| | | 1 7 | 1 8 | 1 9 | 2 0 | 2 1 |
| 表層および裏層 | 配合量 | a 1 : 6 0 | a 5 : 1 0 0 | a 6 : 1 0 0 | a 7 : 1 0 0 | a 8 : 1 0 0 |
| | | b 4 : 4 0 | | | | |
| | | c 1 : 0.50 | c 1 : 0.70 | c 1 : 0.70 | c 1 : 0.70 | c 1 : 0.70 |
| | | c 2 : 0.10 | c 2 : 0.15 | c 2 : 0.15 | c 2 : 0.15 | c 2 : 0.15 |
| 中間層 | 配合量 | d 1 : 3 0 | d 1 : 1 0 0 | d 1 : 1 0 0 | d 1 : 1 0 0 | d 1 : 1 0 0 |
| | | d 3 : 5 5 | | | | |
| | | d 4 : 1 5 | | | | |
| 表／中間／裏層比 | | 20/60/20 | 10/80/10 | 10/80/10 | 10/80/10 | 10/80/10 |
| 引張弾性率 (MPa) | | 1, 7 0 0 | 1, 2 8 0 | 1, 9 1 0 | 1, 5 0 0 | 1, 7 0 0 |
| 熱収縮率 (%) | | 4 8 | 4 4 | 3 0 | 4 5 | 3 5 |
| 静止摩擦係数 | | 0. 4 3 | 0. 2 9 | 0. 4 8 | 0. 2 2 | 0. 4 9 |
| 耐ブロッキング性 | | ○ | ○ | △ | ○ | △ |
| インキ剥離率 (%) | | 0 | 0 | 0 | 2 0 | 0 |
| 層間密着性 | | ○ | △ | ○ | △ | ○ |

[0067]

[Table 10]

| | | 比較例 | | | | |
|-------------|-----|-------------|-------------|-------------|-------------|-------------|
| | | 8 | 9 | 10 | 11 | 12 |
| 表層および裏層 | 配合量 | a 3 : 1 0 0 | a 4 : 1 0 0 | a 1 : 1 0 0 | a 1 : 1 0 0 | a 1 : 4 0 |
| | | | | | | b 1 : 6 0 |
| | | c 1 : 0.70 | c 1 : 0.70 | c 1 : 0.05 | c 1 : 0.70 | c 1 : 0.70 |
| | | c 2 : 0.15 | c 2 : 0.15 | c 2 : 0.03 | c 2 : 0.60 | c 2 : 0.15 |
| 中間層 | 配合量 | d 1 : 1 0 0 | d 1 : 1 0 0 | d 1 : 1 0 0 | d 1 : 1 0 0 | d 1 : 1 0 0 |
| 表／中間／裏層比 | | 10/80/10 | 10/80/10 | 10/80/10 | 10/80/10 | 10/80/10 |
| 引張弾性率 (MPa) | | 970 | 1,990 | 1,530 | 1,520 | 1,990 |
| 熱収縮率 (%) | | 45 | 17 | 45 | 42 | 15 |
| 静止摩擦係数 | | 0.30 | 0.41 | 0.85 | 0.10 | 0.30 |
| 耐ブロッキング性 | | ○ | ○ | × | ○ | ○ |
| インキ剥離率 (%) | | 0 | 0 | 0 | 100 | 0 |
| 層間密着性 | | ○ | ○ | ○ | × | ○ |

[0068]

[Effect of the Invention]The heat contraction nature film using the block copolymer composition thing of this invention, Since it excels in rigidity, heat contraction nature, slippage, blocking resistance, and printing nature, and the heat contraction nature multilayer film which used for the outer layer the film which consists of this block copolymer composition thing further holds the above-mentioned characteristic and it excels in the adhesion between layers, These films can be used as various films for a package, such as a label, a cap seal, etc. which performed various printings.

[Translation done.]